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STATICS AND KINETICS OF CAESIUM SORPTION BY THE NICKEL-POTASSIUM FERROCYANIDES BASED ON HYDATED TITANIUM AND ZIRCONIUM DIOXIDES FROM AQUEOUS MEDIA

Abstract. Optimization of the synthesis of the mixed nickel-potassium ferrocyanide based on hydrated titanium dioxide has been realized. The influence of the conditions of synthesis of the sorbents on the elemental composition, surface texture, statics and kinetics has been shown. The synthetic technique was used to prepare sorbents based on hydrated titanium dioxide carrier. The influence of the chemical properties of the carrier on sorption behaviour of the ferrocyanides was determined.

Keywords: radiocaesium, inorganic sorbent, titanium hydroxide, zirconium hydroxide, nickel-potassium ferrocyanide, static, kinetics.

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СТАТИКА И КИНЕТИКА СОРБЦИИ ЦЕЗИЯ ИЗ ВОДНЫХ СРЕД ФЕРРОЦИАНИДАМИ НИКЕЛЯ-КАЛИЯ НА ОСНОВЕ ГИДРАТИРОВАННЫХ ДИОКСИДОВ ТИТАНА И ЦИРКОНИЯ

Аннотация. Описана оптимизация синтеза смешанного ферроцианида никеля-калия на основе гидратированного диоксида титана. Показано влияние условий синтеза сорбентов на их элементный состав, текстуру поверхности, статику и кинетику сорбции. Методика синтеза была использована для получения сорбента на основе гидратированного диоксида титана. Определено влияние химических свойств носителя на сорбционное поведение ферроцианидов.

Ключевые слова: радиоцезий, неорганический сорбент, гидроксид титана, гидроксид циркония, ферроцианид никеля-калия, статика, кинетика.

Introduction

New inorganic sorbents: thin-layer nickel-potassium ferrocyanides based on hydrated titanium dioxide (T-55 sorbent) and hydrated zirconium dioxide (T-35* sorbent) were prepared and the influence of the synthetic conditions on sorption characteristics towards caesium was studied [1]. Granular hydrated titanium dioxide (T-5 sorbent) and hydrated zirconium dioxide (T-3 sorbent) produced by CJSC CSI "Termoxid" (Zarechny City) were used as a carrier for the thin-layer sorbents. The choice of the carrier is explained by its high radiation and chemical stability, high porosity and the large surface area, together with an organized manufacture that will allow new types of sorbents to be released quickly. The initial carrier materials cannot be used independently as sorbents for caesium because T-3 sorbent does not have specificity towards this radioactive nuclide, and the low specificity of the type T-5 sorbent makes its application for caesium extraction unsuitable.

The properties of inorganic sorbents are determined by their chemical composition, pore structure, and the degree of perfection of the lattice of the sorption material. Modifying the porous structure of the material or changing of the chemical nature of surface of the sorbent will allow the regulation and improvement of their sorption properties. As it is shown in [2], the T-55 sorbent can be used for caesium separation from such extreme media as 8 M nitric acid.

Not only the static characteristics of a sorbent, for example the static exchange capacity and distribution coefficient, but also its kinetic characteristics are very important for the processing of liquid radioactive wastes, because difficulties of pore-diffusion limiting their application are observed for the majority of granular inorganic materials for the sorption of radioactive nuclides. Every phase of the synthesis has an influence on sorption-kinetic characteristics of the inorganic sorbents. Exposure of such influences will permit the positive synthesis of inorganic sorbents with predetermined sorption and kinetic characteristics.

Experimental

The following thermal and chemical modifying techniques were used for preparation of mixed nickel-potassium ferrocyanides:

1) thermal treatment in order to increase the mechanical stability;

2) saturation of the carrier by Ni^{2+} ions under static conditions;

3) treatment of the carrier saturated by Ni^{2+} ions with $K_4Fe(CN)_6$ solution to prepare mixed nickel-potassium ferrocyanides.

As a result of these techniques a new active sorption phase of mixed nickel-potassium ferrocyanide is formed on the surface and in the pore space of the matrix of the inorganic material-carrier previously prepared and calcined.

The influence of the conditions of synthesis on the elemental composition, surface texture and sorption properties was studied for samples of T-55 sorbent.

Kinetic experiments were made under the conditions of limited volume: to a sample of tap water (100 mL) containing 0.01 mg L^{-1} caesium at pH = = 7.80 was added 50 mL of sorbent. At absorption occurs under conditions of the limited volume the change of caesium concentration influences the rate and position of equilibrium. For this reason the experiment was carried out under well-mixed conditions with the solution stirred at 490 rpm. At this speed we can consider that the concentration of sorbate is constant at all points in the solution; and on the surface of the solution we do not consider the influence on diffusion of the interface.

A similar synthetic technique was used using another type of carrier: hydrated zirconium dioxide and this allowed a study of the influence of type of carrier on the static characteristics of the sorbent. To study the statics of caesium interphase distribution the following parameters were used: tap water labeled by Cs-137; volume $V = 50$ mL, sorbent weight $m = 20$ mg, pH = 7.8.

Results

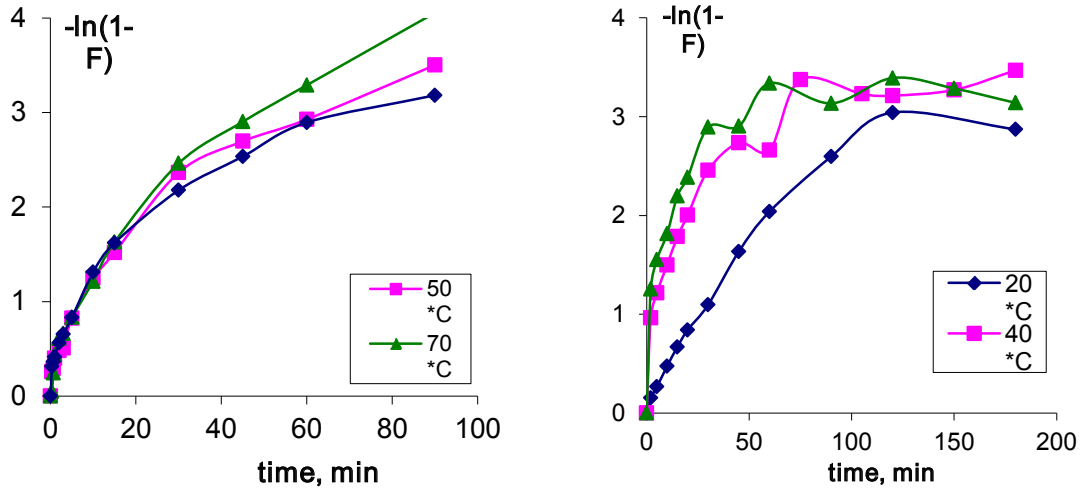
Two samples of T-55 sorbent contained varying quantities of added nickel in the structure after the first stage of modification (sample 1: 14 mg of Ni/g, sample 2: 28 mg of Ni/g) were used to establish of influence of conditions of chemical modification on the formation and surface structure of a T-55 sorbent. The experimental conditions used to carry out of the second stage of modification were identical. The elemental composition of the prepared samples (Table 1) was carried by an X-ray fluorescent spectrometer with polarized radiation "XEPOS" produced by SPECTRO.

The surface of the carrier and the modified samples was examined using a scanning electronic microscope (SEM) (LEO — 420) at a magnification x10000. Size distribution curves of particles visible on the surface were constructed for the samples. Most of the particles had the correct round shape and in those cases where the particle had other shapes, the diameter was accepted as the smallest size of its observable projection. The distribution curves obtained have been described by logarithmically

Table 1

Chemical composition of samples of T-55 sorbent

Sorbent	Content of elements, mg g-1 of sorbent			Molar ratio		Colour of sample
	K	Fe	Ni	K/Ni	Fe/Ni	
sample 1	7.6 ± 1.4	13 ± 3	4.7 ± 1.1	2.38	2.75	dark blue
sample 2	28.1 ± 3.8	17.0 ± 2.1	15.9 ± 1.8	2.66	1.12	green



a) Sample 3 b) Sample 4

Fig. 1. Kinetic dependences of sorption of caesium by mixed nickel-potassium ferrocyanide hydrated titanium dioxide carrier

Table 2

Kinetic characteristics of samples of T-55 sorbent

Sorbent		Sample 3		
		20	50	70
Apparent rate constant, min-1	1st section	0.390 ± 0.270	0.370 ± 0.200	0.450 ± 0.152
	2nd section	0.060 ± 0.016	0.066 ± 0.012	0.066 ± 0.006
	3rd section	0.017 ± 0.012	0.019 ± 0.003	0.026 ± 0.002
Half-exchange time, s.		210	256	208
Diffusion coefficient, $m^2 s^{-1}$	1st section	1.48·10−11	1.41·10−11	1.72·10−11
	2nd section	2.31·10−12	2.61·10−12	2.62·10−12
	3rd section	6.3·10−13	7.11·10−13	1.00·10−12
Sorbent		Sample 4		
		20	40	60
Apparent rate constant min-1	1st section	0.041 ± 0.005	~ 0.48	~ 0,63
	2nd section	0.025 ± 0.007	0.052 ± 0.007	0.057 ± 0.009
	3rd section	0.004 ± 0.002	0.006 ± 0.004	0.002 ± 0.003
Half-exchange time, s.		960	110	60
Diffusion coefficient, $m^2 s^{-1}$	1st section	5.92·10−15	4.08·10−14	1.03·10−13
	2nd section	4.94·10−14	5.59·10−13	1.92·10−13
	3rd section	2.81·10−14	3.31·10−14	7.87·10−15

Table 3

Values of activation energy (E) for caesium sorption by samples of T-55 sorbent

Sorbent	Sample 3			Sample 4		
	1st section	2nd section	3rd section	1st section	2nd section	3rd section
E (kJ mol^{-1})	0.6	2.6	5.5	56.2	50.3	–

normal distribution whose parameters were determined using the built — in functions of Excel of a package of applied programs of Microsoft Office.

The average particle diameter on the sorbent's surface was: 165 ± 5 nm for the T-5 sorbent-carrier; 201 ± 8 nm for Sample 1, and 150 ± 8 nm for Sample 2. It is obvious, that average diameter of particles of Sample 2 is less those of the sorbent-carrier and Sample 1, and thus the electronic microscopic data reveal the presence on this sample's surface of large formations having a size up to 5000 nm in a densely packed texture.

For Samples 1 and 2 under identical experimental conditions the values of the caesium equilibrium distribution coefficients were: 10 $^{(5,6\pm1,0)}$ mL g^{-1} and 10 $^{(3,92\pm0,66)}$ mL g^{-1} respectively.

To study the influence of the duration of the first stage of chemical modification on the kinetic characteristics of the T-55 sorbent Samples 3 and 4 were prepared. The nickel content of the solid phase was 15 mg g^{-1} sorbent, the duration nickel saturation was 1 and 5 days respectively. The results of the kinetic dependences of the sorption of caesium from tap water by the samples prepared at different temperatures are shown in Fig. 1.

These kinetic curves, show three sections with different rates of cesium sorption, a regular sorption rate dependency on temperature is shown for Sample 4 which is absent for Sample 3. The apparent rate constants for caesium sorption for all the designated sections and also the related diffusion coefficients are shown in Table 2. Values of activation energy are included in Table 3.

Apparent rate constants of caesium sorption were determined in terms of kinetic curves using the least-squares method. For the description of the experiment results we have used the models of the diffusion from the limited volume into a spherical body. The calculation of diffusion coefficients was made using a model of pore-diffusion kinetics [3, 4]:

$$F = 1 - \frac{6}{\pi^2} e^{\frac{-\pi^2 \overline{D}t}{R^2}}$$

where F is the extent of attainment of sorption equilibrium and F_0 is a criterion of the loudness ($F_0 = Dt/R^2$)[2]. The chosen models are consistent with the experimental kinetic curves.

The activation energy for caesium sorption for Sample 3 was determined using the apparent rate constants of reaction k; E_1 and E_2 values were calculated based on two pairs of temperatures (20–50 and 50–70 ºC) using the following equation:

$$E = \frac{R \cdot \ln(k_2 / k_1)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

where E = activation energy of reaction, kJ mol^{-1}; T_1, T_2 = temperatures at which chemical reaction was carried out; k_1, k_2 = apparent rate constant of reaction at temperatures T_1 and T_2 respectively.

Values of activation energy E were calculated as arithmetic means of values E_1 and E_2. For Sample 4 the activation energy was calculated using temperature dependence of the diffusion coefficients assuming that this dependence is described by an equation similar to Arrhenius equation:

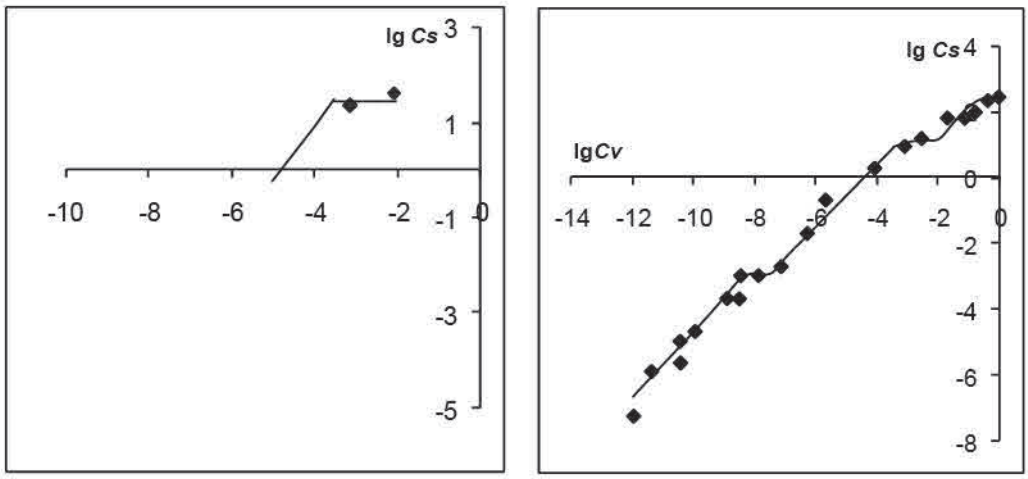
$$D = D_0 \cdot e^{\frac{E}{RT}}.$$

Caesium sorption isotherms with T-55 sorbent (Sample 1) and T-35* using co-ordinates "lg *Cs* — lg *Cv*" over a wide range of concentrations are shown in Fig. 2. *Cs* and *Cv* are equilibrium concentrations of caesium in a sorbent (mg g^{-1}) and in a solution (mL g^{-1}) respectively. It is obvious from Fig. 2 that the caesium sorption isotherms obtained under identical conditions on different types of carriers, possess different profiles, and hence it is possible to assume that the sorbents possess different sorption centres. Each part of the isotherm characterizes a certain type of sorption centres, and in turn each centre is characterized by its value of distribution coefficient and static exchange capacity.

It is possible to assume, that the difference in the nickel content in the structure of a solid phase has led, during the second stage of modification, to a different degree of supersaturation of the solution with K_2Ni [Fe $(CN)_6$]. This increase in the degree of supersaturation leads to an increase in the quantity of fine particles which grow together in dense and poorly permeable structures that are found in Sample 2.

Differences in the surface texture of the samples also influence their sorption properties: leading to differences in the distribution coefficients of caesium sorption observed for Samples 1 and 2. It is possible to assume, that in dense sorption phase of Sample 2 some of sorption centers can be inaccessible to caesium ions and this results in a decrease of specificity of the sorbent.

The results of the experiment mathematical treatment have shown that a change of the nickel saturation time of hydrated titanium dioxide from 5 days to only 1 after the modification, leads to the formation of sorbents with sorption centres in different locations and different accessibility. The rate constants of sorption defined for Sample 3 are 10 times higher than for Sample 4. The difference in diffusion coefficients shows that some of the sorption centres for Sample 4 are situated deeper than in Sample 3 and this causes much greater difficulties for diffusion.



a) hydrated zirconium dioxide (T-35* carrier). b) hydrated titanium dioxide (T-55 carrier)

Fig. 2. Caesium sorption isotherms by mixed nickel-potassium ferrocyanide on various carriers

Discussion

It is obvious from data presented in Table 1 that a part of nickel is washed away from the carrier during treatment of the samples with K_4Fe $(CN)_6$ solution. However the nickel content of Sample 2 both before and after carrying out the second stage of modification exceeds the content in Sample 1. Furthermore, the molar ratios K/Ni and Fe/Ni do not correspond to the stoichiometry of the chemical compound K_2Ni [Fe $(CN)_6$], and is most likely to be connected to the partial formation of titanium ferrocyanide together with mixed nickel-potassium ferrocyanide.

We have defined the difference not only in terms of the kinetic characteristics of sorbents but also in the kinetic mechanisms. If for Sample 3 the sorption is limited by the diffusion of cesium into the pores of a different size, than in Sample 4 the chemical reaction brings an additional contribution. The observation that the experiment energy of activation is ~56 kJ mol^{-1} allows this suggestion to be made.

The experimental results also show that chemical nature of the carrier influences the formation of the nickel-potassium ferrocyanide phase. T-35* based on hydrated zirconium dioxide carrier has only one type of sorption

centre with a Henry distribution coefficient of caesium of $K_d = 10^{(4.5 \pm 0.4)}$ mL g^{-1}, and a static exchange capacity (SEC) not exceeding 34 mg $g^{-1.}$

Meanwhile the T-55 sorbent based on hydrated titanium dioxide prepared under similar conditions is a poly-functional sorbent. The step character of the isotherm "lg *Cs* — lg *Cv*" with three linear section concluding with an area of saturation for the given type of sorption centers confirms it. The maximum value of the caesium equilibrium distribution coefficient for this type of sorbent $K_d = 10^{(5.6 \pm 1.0)}$ mL g^{-1} is realized when the initial solution concentration of caesium is less than 10^{-3} mg L^{-1}; in solutions with caesium concentrations up to 1 mg L^{-1} $K_d = 10^{(4.2 \pm 0.6)}$ mL g^{-1}; and for solutions with the even larger concentrations $K_d = 10^{(2.4 \pm 0.1)}$ mL $g^{-1.}$ It is possible to assume, that the first type of sorption centre is connected to the K_2Ni [Fe $(CN)_6$] phase and the second type probably belongs to chemical compounds such as normal titanium ferrocyanide or mixed titanium-potassium ferrocyanide. The X-ray structure analysis data currently available do not allow final conclusions to be drawn. The third part of the isotherm has a significant deviation of the slope from unity (0.48 ± 0.08), while the capacity of the sorbent is not less than 267 mg g^{-1}, that essentially exceeds the capacity of T-5 sorbent alone [1]. It is probable, that precipitation of Cs_2Ni [Fe $(CN)_6$] takes place in the pores of the sorbent during its contact with a solution containing a high concentration of caesium. Such an opportunity is caused by the presence of molecularly adsorbed K_4Fe $(CN)_6$ and unreacted hydrated nickel ions during the second stage of modification. The probability of Cs_2Ni [Fe $(CN)_6$] precipitation has been additionally corroborated by experiments of the caesium sorption kinetics from tap water containing K_4Fe $(CN)_6$ by T-5 sorbent and T-5 sorbent saturated with nickel. In the first case absence of caesium sorption was shown whereas in the second case the loss of caesium from the solution at different concentrations of K_4Fe $(CN)_6$ was up to 40 %.

Nickel-potassium ferrocyanides based on hydrated zirconium dioxide are inferior to ferrocyanides based on hydrated titanium dioxide in their specificity towards caesium.

Conclusions

It has been shown, that changes of conditions of synthesis results in the formation of an active sorption phase having various chemical compounds and different surface structures that are reflected in differences between the static and kinetic characteristics of the sorbents. Optimization of a synthetic method has allowed the preparation of samples of sorbents possessing increased specificity, high capacity and improved kinetic characteristics. The influence of the type of carrier on the sorption properties of the prepared nickel-potassium ferrocyanides was established.

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